

## Plasma: the way to engineer the surface of advanced materials

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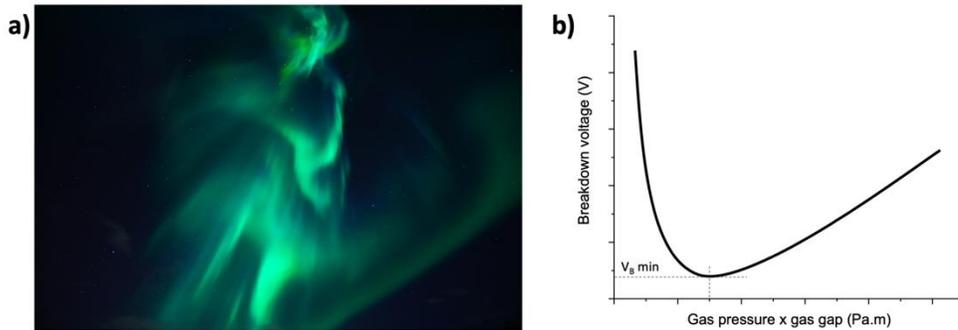
### 1. Introduction

The surface properties of a material constitute the success key for adding value in almost all industrial applications by controlling the performance of the final product and the way it interacts with the surrounding environment. As an example, issues of corrosion, adhesion, and biocompatibility can strongly affect the quality of an object when the surface is not considered a critical step in the production process. In this context, surface modifications such as wet chemicals (*e.g.* with acids, alkalis, grafting), mechanical (*e.g.* patterning, grinding, and blasting), and plasma treatments (*e.g.* corona, flame assisted plasma) are commonly applied to overcome these issues [1]. This article is dedicated to demystifying the principles of plasma surface modifications, as well as the potential and the challenges offered by this technique.

*What is plasma?* Plasma is an ionized neutral gas containing a mixture of electrons, ions, neutrals, and photons [2]. The plasma state constitutes over 99% of the universe. Some examples are thunderbolts, nebula clouds, and stars (Figure 1a). In a laboratory, there are different methods to produce plasma [3]. One of them is by heating a gas (to the order of thousands of degrees) in a process like what occurs in the stars. This causes collisions between the molecules, and ultimately produces free electrons and ions. By exposing the gas to electromagnetic radiation (*e.g.* radio frequency, microwaves, X-rays) it is also possible to induce a photoionization process which results in an electrically charged state. The latter naturally happens in the Borealis Aurora. One of the most common methods used in the laboratory implies an electric field (usually order of kV/cm) between two electrodes to polarize the gas. This is the working principle of the neon lights and fluorescent bulbs.

*How can plasma modify surfaces?* When a surface is in contact with plasma, the highly reactive mix of energetic species (*i.e.* ions, radicals) interacts with the surface. For example, noble gases produce

non-reactive plasmas and they mainly induce changes in surface roughness. This type of plasma is commonly used for removing surface contaminants. On the other hand, reactive plasmas (e.g. nitrogen, hydrogen, air, hexafluoroethane) interact with the surface by introducing new functional groups or by producing thin films. So, depending on the gas source and other parameters, plasma treatments offer the possibility to change the physico-chemical properties on the first nanometers of a wide variety of substrates (e.g. polymers, wood, ceramic, metals) without affecting the bulk properties [2].



**Figure 1. a) Example of natural plasma. b) Graphical representation of Paschen's law.**

*What are the parameters affecting the plasma?* The most important parameters that can strongly influence the physical regime of the process are the geometry/configuration of the electrodes in the reactor, the electrical conditions (i.e. power supply, voltage, and frequency of the electrical field), the gas precursor, and the pressure. Using Paschen's law, it is possible to establish the value of the voltage (i.e. breakdown voltage) needed to initiate plasma, at a specific pressure, when two electrodes are separated by a precise length (i.e. gap length) [4]. Figure 1b depicted the evolution of the voltage as a function of the other parameters. One can note that at low pressures and low gas lengths, it is easier to start plasma. In this sense, different physical regimes, therefore different plasma surface modifications, occur by working at low pressure (1 mTorr - 1 Torr) and at high pressure ( $\geq 760$  Torr).

*Why do we need different physical regimes?* In the 20th century, low-pressure plasma became widely used in industry because the rise of microelectronics and optical applications [4]. However, in the last decade, there has been a rapidly growing interest towards atmospheric plasma systems. In these systems, the elimination of expensive vacuum equipment offers the possibility to integrate surface modification in a chain manufacture process and treat a higher amount of substrate in less time [5]. Nevertheless, low-pressure plasma, working with batch processes, plays a crucial role when purity and homogeneity of the gaseous reactions are essential for surface modifications [6].

*What are the challenges of plasma treatments?* Beyond the parameters affecting the plasma it is important to point out that different materials have different requirements in terms of how susceptible their surfaces are prone to modification. For example, fluoropolymers ( $C_xF_y$ ) have high chemical resistance attributed to the highly electronegative fluorine sheath that protects the carbon backbone from chemical attack [7]. Although this intrinsic inertness makes them an ideal polymer in bioengineering and chemical industry applications, its development and modification by plasma treatment still present some challenges [8].

Herein, two different plasma processes are presented as examples of their versatility to treat fluorocarbon polymers. Atmospheric plasma is used to modify a fluoropolymer to promote higher film adhesion, whereas low-pressure plasma is used to develop a fluoropolymer coating.

## 2. Materials and Methods

### a. Substrates

A fluoroethylene propylene (FEP, from Holsco Europe) film of 0.127 mm in thickness was modified at atmospheric pressure plasma to introduce polar groups on its surface and enhance its adhesion to other materials. Alternatively, a stainless steel (SS316L, from Sigma Aldrich) substrate was treated with low-pressure plasma to grow a fluorocarbon polymer coating.

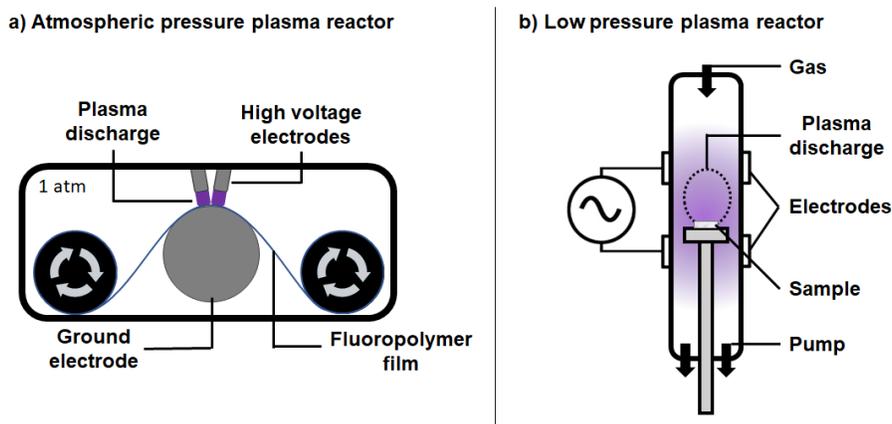


Figure 2. Schematic representation of a) atmospheric pressure and b) low-pressure plasma reactors.

### b. Plasma Reactors

The plasma surface treatments were performed in two different reactors, as shown in Figure 2. The atmospheric plasma reactor is shown in Figure 2a. It works at 760 Torr of pressure using a radio frequency (RF) power supply. The discharge cell consists of two parallel electrodes made of aluminium, among which

the air flows. The polymer film (substrate) was placed on the grounded electrode and it acts as a dielectric barrier. The film can be passed through the discharge at different speeds [8]. On the other hand, the low-pressure reactor (Figure 2b) consists of a chamber with a sample holder connected to a power generator, turbomolecular pump, and a gas supply. The process is carried out at 0.7 Torr using  $C_2F_6$  as a gas precursor injected inside the chamber and ionized with a RF power supply [9].

### *c. Characterization Techniques*

To understand the effect of the plasma surface treatments, X-ray photoelectron spectroscopy (XPS), contact angle (CA), and atomic force microscopy (AFM) were used to obtain information of the materials surface's physico-chemistry. XPS provide information on the surface chemistry by the detection of photoelectrons emitted from the sample after X-ray irradiation. Each analysis gives a set of peaks at characteristic binding energies which are directly correlated to a specific element of the material's surface, with a penetration depth of approximately 5 nm. The contact angle (CA) is the parameter that measures the wettability, which determines the affinity between a liquid and a solid surface. When there is a strong attraction between the liquid and the solid, the CA will be  $< 90^\circ$  and  $> 90^\circ$  for lower attraction. Finally, using AFM it is possible to study the changes in surface morphology at nanometric level. AFM operates with a sharp tip to scan the surface of the sample and a laser beam to detect cantilever deflections towards or away from the surface. The resulting variations during scanning are plotted as a function of the position of the tip to create an image.

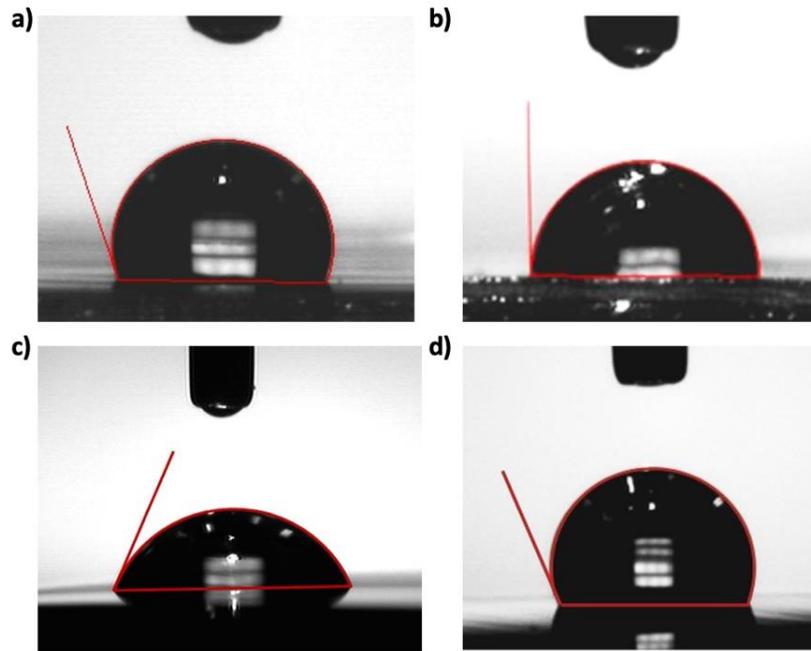
## **3. Results and Discussion**

XPS analysis on Table 1 shows the presence of carbon and fluor for untreated FEP samples. The calculated F/C ratio is close to 1.8. After the atmospheric plasma treatment, the F/C ratio decrease to 1.5. Also, the addition of nitrogen ( $2.3 \pm 0.3$  at. %) and oxygen ( $2.0 \pm 0.4$  at. %) are observed on the surface. This result indicates a defluorination of the FEP after the plasma treatment. The corresponding CA shows a decrease from  $111 \pm 1^\circ$  (untreated, Figure 3a) to  $90 \pm 5^\circ$  after plasma treatment (Figure 3b). This decline is attributed to the presence of nitrogenated and oxygenated groups on the surface which have strong interactions with water. Finally, Figures 4a and 4b show the morphology of untreated and plasma-treated FEP. No surface changes are visible after the plasma process at atmospheric pressure. The measured roughness remains close to  $8.4 \pm 0.3$  nm which is similar to the one obtained with the untreated sample ( $8.0 \pm 0.3$  nm).

**Table 1. XPS survey. \*Reported values from [9].**

Process		Atmospheric pressure plasma		Low-pressure plasma	
		Untreated	Treated	Untreated*	Treated
Atomic percentage (at. %)	C1s	35 ± 3	38.6 ± 0.4		23 ± 3
	F1s	65 ± 3	58.1 ± 0.5		31 ± 3
	N1s		2.3 ± 0.3		
	O1s		2.0 ± 0.4		34 ± 2
	Fe2p3			66	3 ± 1
	Cr2p3			18	2.1 ± 0.4
	Ni2p3			10	2.5 ± 0.4
	Others			6	5 ± 1

Stainless steel has a reported composition of 66 at. % Fe, 18 at. % Cr, and 10 at. % Ni [9]. After low-pressure plasma, XPS survey reveals that treated surface is composed of 31 ± 3 at. % fluor and 23 ± 3 at. % carbon (see Table 1). The obtained F/C ratio is 1.4. In comparison, pristine polytetrafluoroethylene (PTFE) has a reported F/C ratio of 1.86 [10]. The difference for the F/C ratio is attributed to the high oxygen content (34 ± 2 at. %) on treated sample. Their presence led to the preferential formation of C=O and C-O functional groups instead of CF<sub>x</sub> groups. In addition, the presence of metallic traces on the modified sample highlights the nanometric scale of the coating obtained with this short-time treatment (5 min). For these reasons, one can conclude that a thin film PTFE-like polymer covers the SS316L surface after the plasma process. It is interesting to note that the CA measurements (Figures 3c and 3d) exhibit a strong change depending on the surface analyzed. An increase in the water CA, from 66.6 ± 0.8° to 112 ± 1° is observed after the plasma treatment. This is correlated to the incorporation of the fluorinated groups and it is in accordance with reported PTFE values (104 – 110°) [7,9,10]. Lastly, Figures 4c and 4d show the surface morphology of untreated surface and fluorocarbon layer. The measured roughness indicates an increase of the value, from 0.7 ± 0.5 nm, for untreated sample, to 2.1 ± 0.2 nm. The low value obtained after the plasma modification highlights the homogeneity of the plasma polymerization at low pressure.



**Figure 3. Contact angle images of fluorocarbon polymers (a) before and (b) after atmospheric pressure treatment and (c) before and (d) after low-pressure plasma.**

The different changes in the samples obtained by using the different plasma processes were clearly highlighted in the previous paragraphs. Atmospheric pressure plasma was used to treat a FEP film without the deposition of material. The modifications have enhanced the wettability of the surface by introducing polar groups on the surface. However, the surface morphology did not change and the surface chemistry of the FEP film remained covered by carbon and fluor functional groups. In this sense, a grafting process was performed by using the plasma treatment in a non-polymerization gas at atmospheric pressure.

On the other hand, low-pressure plasma was used to grow a  $CF_x$  polymer as a protective and an antiadhesive coating on a SS316L substrate. The thickness and the F/C efficiency of the deposited fluorocarbon polymer were correlated to the parameters used. A completely different chemical composition and wettability were observed before and after plasma treatment. The surface roughness increased due to the deposition of a new fluorocarbon coating in the presence of a polymerization gas.

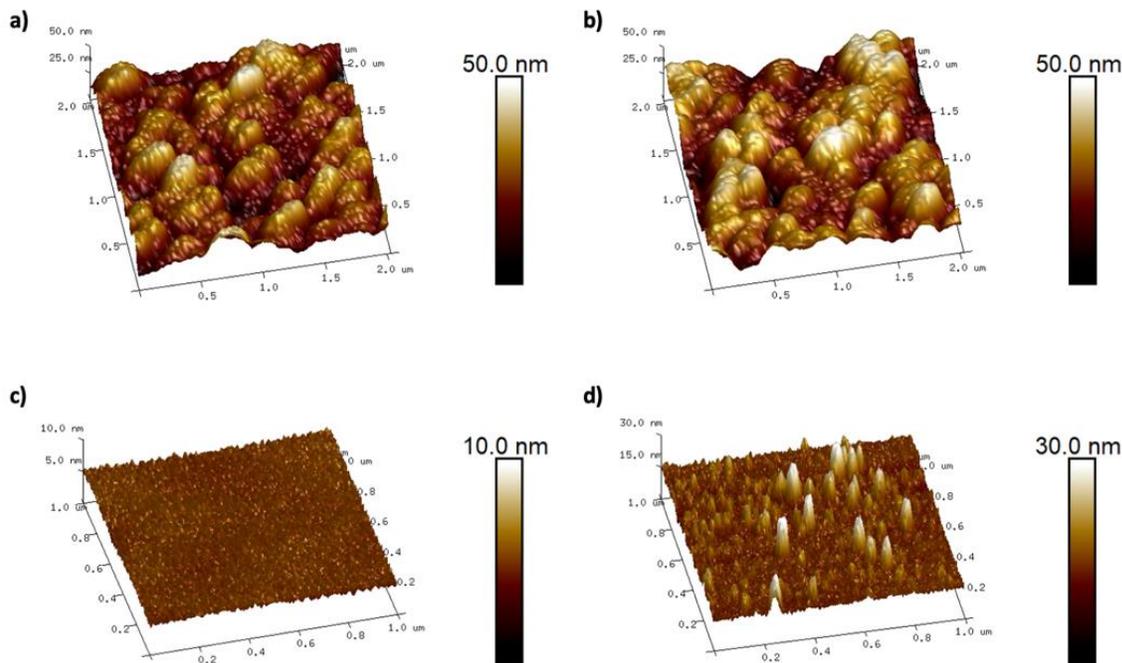


Figure 4. Surface images of fluorocarbon polymers (a) before and (b) after atmospheric pressure treatment and (c) before and (d) after low-pressure plasma.

#### 4. Conclusion

Atmospheric pressure and low-pressure plasma were proven to be efficient techniques for the deposition and the modification of fluorocarbon polymers. Through the study of surface morphology, composition, and wettability it was possible to highlight the different physico-chemical modifications obtained with two physical regimes. The transformed surfaces demonstrated the high versatility of plasma on different substrates.

#### 5. Acknowledgments

The authors thank Jacopo Profili, PhD, and Pascale Chevallier, PhD, for their scientific support.

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